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(54) Method for Producing White Electrically Conductive Zinc Oxide

(72) Hayashi, Takao - Japan ;
Sato, Norihiro - Japan ;
Omotani, Chikara - Japan ;
Hosoi, Manabu - Japan ;
Kasahara, Nobuyoshi - Japan ;
Rudolph Günther - Japan ;
Griebler, Wolf-Dieter - Japan ;
Hocken, Jorg - Japan ;

(73) Metallgesellschaft Aktiengesellschaft - Germany (Federal Republic of) ;
Mitsui Mining & Smelting Co., Ltd. - Japan ;

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(57) 3 Claims

Notice: The specification contained herein as filed

ABSTRACT OF THE DISCLOSURE:

A method for producing white electrically conductive zinc oxide comprising reacting an aqueous alkali solution with a solution which contains a water-soluble zinc compound and at least one water-soluble metal compound selected from the group consisting of tin, gallium, indium and aluminum compounds to form co-precipitates so that the amount of at least one member selected from the group consisting of tin oxide, gallium oxide, indium oxide and aluminum oxide determined after calcination of the co-presipitates ranges from 0.005 to 5.0 parts by weight to 100 parts by weight of zinc oxide, while simultaneously feeding these two solutions to a reaction zone so that pH value of the reaction solution is maintained at a desired value falling within the range of from 6 to 12.5; and then calcining the resultant co-precipitates in a reducing atmosphere.

The embodiment of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing white electrically conductive zinc oxide comprising reacting an aqueous alkali solution with a solution which contains a water-soluble zinc compound and at least one water-soluble metal compound selected from the group consisting of tin, gallium, indium and aluminum compounds to form co-precipitates so that the amount of at least one member selected from the group consisting of tin oxide, gallium oxide, indium oxide and aluminum oxide determined after calcination of the co-presipitates ranges from 0.005 to 5.0 parts by weight to 100 parts by weight of zinc oxide, while simultaneously feeding these two solutions to a reaction zone so that pH value of the reaction solution is maintained at a desired value falling within the range of from 6 to 12.5; and then calcining the resultant co-precipitates in a reducing atmosphere.

2. The method as set forth in claim 1, wherein the calcination temperature ranges from 400 to 550°C.

3. The method as set forth in claim 1, wherein the calcination temperature ranges from 400 to 500°C.

The present invention relates to a method for producing electrically conductive zinc oxide excellent in whiteness in a high yield. More specifically, the present invention pertains to a method for producing white electrically conductive zinc oxide useful in the applications listed below: a conductive coating agent used in making electrostatic recording paper and a conductive filler into antistatic paints, rubbers and resins.

(Prior Art)

There have been known a variety of methods for producing electrically conductive zinc oxide such as those listed below. For instance, Japanese Patent Laid Open Corresponding to OLS in Germany (hereunder referred to as "J.P. KOHKAI") Nos. Sho 58-161923, Sho 58-145620, Sho 55-162477, Sho 59-97531, Japanese Patent Publication corresponding to Auslege in Germany (hereinafter referred to as "J.P. KOHKOKU") No. Sho 55-19897 and U.S. Patent No. 3,538,022 disclose methods which comprise adding, to zinc oxide powder, an oxide of at least one metal selected from the group consisting of aluminum, gallium, indium, tin and the like as a dopant to admix them and then heating the mixture at a temperature ranging from 600 to 1200℃ in a reducing atmosphere to calcine the mixture. In addition, there have also been known dry methods such as those comprising heating a mixture of zinc oxide powder and a

dopant in the presence of solid carbon to calcine the mixture; wet methods such as those disclosed in J.P. KOHKAI Nos. Sho 62-35970, Sho 61-86421 and Sho 61-40338, which comprise neutralizing a mixture of a solution of a water-soluble zinc compound and a solution of a water-soluble compound of the aforesaid metal with an aqueous solution of an alkali hydroxide or an alkali carbonate or the like to form co-precipitates and heating and calcining the co-precipitates at a temperature of 500 to 1000 ℃ in nitrogen atmosphere or in a reducing atmosphere after washing, drying of preheating the co-precipitates; and the like.

(Problems to be Solved by the Invention)

However, in order to impart sufficient electric conductivity to a calcined product a dry method is necessary to perform calcination at an elevated temperature under a reducing atmosphere. This is accompanied by volatilization of zinc oxide due to reduction. Consequently, the yield of the desired product is remarkably lowered. Moreover, there is sometimes observed secondary sintering of the products during calcining step.

On the other hand, in all of the conventional wet methods for producing electrically conductive zinc oxide, neutralization is performed in a batchwise operation and more specifically an aqueous solution of an alkali hydroxide or an alkali carbonate is gradually added to an aqueous solution of a water-soluble compound of zinc and a water-soluble compound of a metal as a

dopant so that a final pH of the reaction system falls within the range within which zinc and the like cause precipitation. In such a method, pH at the beginning of the neutralization differs from that at the final stage. Therefore, it is difficult to co-precipitate two or more of products having different rates of hydrolysis or rates of dissolution in a desired ratio so as to achieve a homogeneous distribution of the product in the solid phase. Accordingly, to impart a desired degree of electric conductivity to the resulting product, it is inevitable to carry out calcination under a reducing condition at an elevated temperature. However, such a calcina tion at an elevated temperature is accompanied by lowering of product yield as a result of volatilization of zinc oxide and further the reducing atmosphere in which the calcination is carried out exerts influence on the product to thus cause partial reduction of the resulting metal oxide, which is in turn accompanied by deposition of metals in a trace amount. This causes the lowering in whiteness of the resultant calcined product.

Accordingly, an object of the present invention is to develop a technique for producing calcined products having a desired electric conductivity with low temperature calcination.

(Means for Solving the Problems)

The inventors of this invention have selected a wet method for producing white electrically conductive zinc oxide powder as a means for solving the problems

which still remain unsolved in the aforementioned conventional methods and have conducted various studies to improve the wet method. As a result, the inventors have found that the co-precipitates serving as a starting material for calcination should have homogeneous compositional distribution to obtain calcined products having practically acceptable electric conductivity with low temperature calcination. The homogeneity of this compositional distribution can be confirmed by analyzing X-ray diffraction spectra of the co-precipitates.

According to the present invention there is provided a method for producing white electrically conductive zinc oxide comprising reacting an aqueous alkali solution with a solution which contains a water-soluble zinc compound and at least one water-soluble metal compound selected from the group consisting of tin, gallium, indium and aluminum compounds to form co-precipitates so that the amount of at least one member selected from the group consisting of tin oxide, gallium oxide, indium oxide and aluminum oxide determined after calcination of the co-presipitates ranges from 0.005 to 5.0 parts by weight to 100 parts by weight of zinc oxide, while simultaneously feeding these two solutions to a reaction zone so that pH value of the reaction solution is maintained at a desired value falling within the range of from 6 to 12.5; and then calcining the resultant co-precipitates in a reducing atmosphere.

Therefore, in the present invention, means for obtaining co-precipitates showing homogeneous compositional distribution, in other words, co-precipitates in which a compound of a metal serving as a dopant is homogeneously distributed throughout the solid phase of zinc oxide are as follows:

(i) An aqueous solution containing a water-soluble

compound of zinc and a water-soluble compound of at least one metal selected from the group consisting of tin, aluminum, gallium and indium;

(ii) An aqueous alkaline solution;

(iii) Both of these solutions (i) and (ii) are simultaneously fed to a reactor;

(iv) The addition of these solutions is performed while controlling the pH value of the water phase of the reaction system to around a desired value falling within the range of from 6 to 12.5, preferably 7 to 12.

In the foregoing method, the term simultaneous addition also embraces the continuous addition and

intermittent addition of the solution containing the zinc compounds and the compounds of other metals defined above and the aqueous alkaline solution so as to maintain the pH value of the liquid phase of the neutralization reaction system to a desired value falling within the predetermined range.

The amount of each component contained in each solution is expressed in the amount to the corresponding oxide based on the composition of the oxidized product obtained after calcination and is selected so that the amount of at least one metal oxide selected from the group consisting of tin oxide, gallium oxide, indium oxide and aluminum oxide ranges from 0.005 to 5.0 parts by weight, preferably 0.005 to 2.0 parts by weight to 100 parts by weight of zinc oxide. In this respect, if the dopant comprises two or more of the foregoing metal oxides, the total amount of these oxides should range from 0.005 to 5.0 parts by weight, preferably 0.005 to 2.0 parts by weight.

The homogeneous co-precipitates formed are filtered, then washed with water to remove impurity ions as low as possible and dried usually at a temperature ranging from 80 to 150 ℃. If the resulting dried precipitates are calcined at a temperature of as low as 400 to 550 ℃, preferably 400 to 500 ℃ in a reducing atmosphere including hydrogen gas, the lowering in whiteness of the calcined product is not observed and the calcined product can be obtained in a high yield. Though, the calcined product

is obtained according to low temper-ature calcination, it has a practically acceptable low electric resistance of the order of 10^{-1} to 10^{3} ohm·cm.

The water-soluble zinc compounds which may be used in the present invention are not restricted to specific ones so far as they provide zinc oxides through calcination. Preferred examples thereof are zinc sulfate, zinc chloride, zinc nitrate, zinc acetate or a mixture thereof since they are easily commercially available.

The water-soluble metal compounds serving as a dopant are not also restricted to specific ones so far as they can provide tin oxide, gallium oxide, indium oxide or aluminum oxide through calcination. From the practical view point, usually employed are at least one chloride, nitrates, sulfates and acetates of the metals constituting the foregoing oxides as well as at least one alkali metal salts of oxoacids of these metals, i.e., stannic acid, gallium acid, indium acid and aluminic acid.

These dopants provide acceptable effects even if they are used alone, but more excellent effects can be achieved if they are added in combination with at least two of them (combined addition). Examples of such combinations are tin oxide/gallium oxide, tin oxide/indium oxide, or aluminum oxide/gallium oxide as expressed in oxides.

The value of pH of an aqueous solution in which zinc ions and metal ions of the dopant coexist, is usually adjusted up to 1.0 so as to avoid hydrolysis prior to the

reaction with an alkali. The concentration of the metal ions in the solutions is not restricted to a specific one so far as it does not exceed the solubility thereof, but it is preferred that the concentration thereof be in the range of from 200 to 500g/1 in a system in which zinc ions and dopant metal ions coexist from the practical point of view.

Examples of alkali metal hydroxides or alkali metal carbonates which are principal components of the alkaline aqueous solution used in the neutralization reaction include sodium hydroxide (caustic soda), potassium hydroxide (caustic potash), ammonium hydroxide (ammonia), sodium carbonate (soda ash), sodium hydrogen carbonate (sodium bicarbonate) and ammonium carbonate. These compounds may be used alone or in combination and are usually used in the form of an aqueous solution.

The most important aspect of the present invention resides in the combination of the following two requirements:

Requirement-1: The neutralization reaction is performed so that the pH value of the neutralization system is maintained at a specific value falling within the range of from 6 to 12.5, preferably 7 to 10;

Requirement-2: The aqueous solution containing a water-soluble zinc compound with a water-soluble metal compound and an

alkaline solution are simultaneously fed to a neutralization reaction system.

The significance of the requirement-1 is as follows:

If the pH value is less than 6, the hydrolysis of the water-soluble zinc compound is insufficient and, therefore, not only the yield of the final product is decreased but also the reaction provides products having high content of impurity, i.e., low quality due to the formation of basic salts as by-products.

On the other hand, if the pH value exceeds 12.5, the electric conductivity of the resultant product is insufficient, in other words, it does not reach a desired level. This is because the hydrolysis of the dopant remains insufficient under such a condition.

If the pH value is controlled to a value falling within the foregoing range, the formation of basic salts can be completely prevented or only a trace amount thereof is formed. Accordingly, almost all the amount of the resulting precipitates can be converted to zinc oxide even if the precipitates are dried at a lower temperature condition of the order of ordinary temperature to 150℃. However, in the conventional methods, the precipitates obtained cannot be sufficiently converted to zinc oxide when the precipitates are dried at such a low temperature. As a countermeasure of this problem, there has been performed preheating at 400 to 700℃ in the air prior to calcination in a

reducing atmosphere. Moreover, a substantial amount of water vapor is generated during the calcination in a reducing atmoshere and hence a large amount of hydrogen is consumed in such conventional methods.

The significance of the requirement-2 is as follows

If the both solutions are simultaneously fed to the neutralization reaction system, selective hydrolysis of the dopant can be prevented.

The formation of co-precipitates having homogeneous compositional distribution can be ensured by co-precipitating water-insoluble or hardly water-soluble compounds formed from both of zinc and the metal in the dopant simultaneously, homogeneously and continuously (this fact was confirmed by analyzing X-ray diffraction patterns).

The significance of the combination of these two requirements is as follows:

Supplementary examinations carried out by the present inventors indicate that gray-colored powder was obtained instead of white electrically conductive powder according to the technique as disclosed in J.P. KOHKAI No. Sho 61-86421 which is barely thought to be a prior art of this invention. This Official Gazette discloses neither the simultaneous addition of the aqueous solution of a zinc compound and a dopant and an aqueous solution of an alkali nor the fact that the reaction is performed while controlling the pH value of the neutralization reaction system at a desired value falling within the range of from 6 to 12.5.

Moreover, the drying operation of the resulting precipitates is carried out at an elevated temperature of the order of 400℃ or 500 ℃ which is almost equal to the calcination temperature and further the calcination in a reducing atmosphere is performed at a temperature of 700 ℃ which is substantially higher than the upper limit of the calcination temperature used in the present invention. The inventors of this invention are the first person to succeed in developing a method capable of imparting practically acceptable electric conductivity to calcined products even if the calcination is performed at a temperature as low as 400 to 500 ℃ . It is of much importance that this success is what the method of this invention can achieve the enhancement of yield of calcined products as well as the improvement in whiteness thereof (prevention of darkening).

The co-precipitates formed through the neutralization reaction comprising the combination of the requirement-1 with the requirement-2 are filtered off according to a known manner, followed by washing the precipitates with water until the electric conductivity of the filtrate becomes at most 300 μ S/cm, drying the precipitates at a temperature ranging from ordinary temperature to 150℃ and then calcining them, without previous pulverization, at 400 to 550 ℃ , preferably 400 to 500 ℃ in a reducing atmosphere containing hydrogen gas.

The product obtained through calcination under a reducing atmosphere is very fragile and, therefore, can easily be formed into fine powder. Since, in the present

invention, the calcination is performed at a very low temperature of as low as 400 to 550°C, volatilization of zinc oxide due to the reduction is very small and hence electrically conductive zinc oxide can be obtained in a high yield. The specific volume resistivity of the white electrically conductive zinc oxide powder obtained according to the process of this invention is usually in the range of from 10^{-1} to 10^{2} ohm.cm and it is very stable to an extent that it hardly varies with time. In most cases, the powder is obtained in the form of approximately spherical shape having an average particle size ranging from about 0.05 to 0.5 micron.

Examples will now be given, sometimes having reference to the attached drawing wherein:

- Fig. 1(a) and Fig. 1(b) are X-ray diffraction patterns of the products obtained in a specific or certain of these Examples. In Fig. 1(a) no diffraction peak assigned to the dopants was observed while in Fig. 1(b) the peak assigned to metallic tin resulting from the dopant was found.

EXAMPLE 1

11.17 kg of zinc chloride (96%), 71.67 g of tin (IV) chloride (98% in purity) (the ratio of addition being 0.593% expressed in the amount of SnO_2 based on the weight of the zinc oxide) and 64.72 g of gallium chloride (99.9% in purity) (the ratio of addition being 0.545% expressed in the amount of Ga_2O_3 based on the weight of the zinc oxide) were dissolved in water and 400 ml of 36% hydrochloric acid to obtain 15 liters of a solution A. The solution A and an NaOH solution (240 g/l in concentration) were simultaneously fed to a reaction system over 180 minutes while maintaining the pH value of the reaction solution at 10 and the reaction

temperature at 60°C to thus obtained co-precipitates. The resulting co-precipitates were filtered off in an ordinary manner, then washed with water until the electric conductivity of the filtrate of

washing liquid became at highest 300μ S/cm and were dried at 105 ℃ in air. The resultant block-like product (about 2 to 30 mm in size) as such was calcined at a temperature of 500℃ for 60 minutes in hydrogen gas atmosphere to thus obtain 6.3 kg of white electrically conductive zinc oxide powder. The powder resistivity of the resultant product was 1.8×10^{0} ohm·cm.

Moreover, the fact that the percentage loss in weight observed during calcination became a value as low as 2% indicates that the precipitates were almost completely converted into zinc oxide during drying.

In this respect, the homogeneity of the compositional distribution of the foregoing dried block was confirmed by X-ray diffraction measurement performed prior to the calcination. The results obtained were illustrated in the Fig.1(a).

The batchwise neutralization of the solution A with the solution B was carried out in the same manner as in the Example-1 to bring the final pH value of the solution to 10. The results were shown in the Fig.1(b) in the purpose of comparison.

Results:

In Fig. 1(a), only the diffraction line of zinc oxide is observed while no diffraction line due to tin oxide or gallium oxide which may possibly co-exist is observed.

On the other hand, in Fig. 1(b), there are observed diffraction lines due to metallic tin between the diffraction lines of zinc oxide (in the vicinity of

2θ = 43.8° and 44.8°).

In Table I there were listed the results obtained.

Discussion

It can be concluded that the diffraction lines due to tin oxide or gallium oxide are not observed as seen from Fig. 1(a), since tin oxide or gallium oxide is homogeneously distributed throughout zinc oxide lattice.

It can be interpreted that the diffraction lines are observed as shown in Fig. 1(b), because a part of tin oxide deposited on the surface of zinc oxide is reduced to metallic tin. This interpretation is also supported by the fact that the resultant product showed dark gray appearance.

The content of chlorine atom in the calcined product was quite low, i.e., 0.01%. Then the change in the powder resistivity of the electrically conductive zinc oxide powder in the air was determined to evaluate storage stability (change with time) thereof. The results thus obtained indicate that the zinc oxide powder is very stable as will be shown below(see Table I also).

days from the beginning:	10	30	120
powder resistivity($\Omega \cdot cm$):	5.4×10^{0}	5.2×10^{0}	4.3×10^{0}

Example 2

The same procedures as in Example 1 were repeated except that the neutralization was carried out so as to maintan the pH value of the liquid phase of the reaction system at 12 to thus obtain 6.25 kg of white electrically

conductive zinc oxide powder. The powder resistivity thereof was 4.0 × 10^{0} ohm·cm. The results obtained are summarized in the following Table I.

Example 3

Various white electrically conductive zinc oxide powder were prepared according to the same procedures as in Example 1 except that the kinds of the water-soluble zinc compounds, the kinds and the amount of dopants, the kinds of alkalis, pH values of reaction systems and calcination temperature utilized were variously changed. The conditions and the results obtained are summarized in the following Table I.

Comparative Example 1 (Addition of Alkali in One Portion)

There were dissolved 52.34 g of zinc chloride (96%), 0.95 g of tin chloride (98%) and 0.47 g of aluminum chloride (95%) in 1.2-liter of water and 37.80 g of sodium carbonate (99.7%) was added to the solution in one portion with sufficiently stirring the system to perform a neutralization reaction. The deposited basic zinc carbonate co-precipitates containing aluminum and tin were introduced into a closely sealed container to adjust the slurry concentration to 300 g/1, the contents of the container was heat-treated at 80 ℃ for 5 hours, followed by filtering off, washing and drying the resulting precipitates. The dried co-precipitates were calcined at 700℃ for 3 hours in hydrogen gas atmosphere to obtain dark gray electrically conductive zinc oxide powder. Its powder resistivity was 4.2× 10^{1} ohm· cm and the yield of the product was 55.7%.

The results was illustrated in the following TableⅡ.

Comparative Example 2

There were dissolved 52.34 g of zinc chloride (96%), 0.96 g of tin (Ⅳ) chloride (98%) and 0.48 g of aluminum chloride (95%)in 1.26 liter of water and 195 cc of an aqueous solution containing 0.217 g of gallium chloride (99.9%), 0.91 g of sodium hydroxide and 37.42 g of sodium carbonate (99.7%) was added to the solution in one portion with sufficiently stirring the system to perform a neutralization reaction. The co-precipitates formed was filtered off, washed with 3 liters of warm water and were introduced into a closely sealed container to adjust the slurry concentration to 300 g/1, the contents of the container was heat-treated at 80℃ for 5 hours, followed by again filtering off the co-precipitates, again washing the same and drying them at 500 ℃ for 3 hours. The dried co-precipitates were calcined at 700 ℃ for 3 hours in hydrogen gas atmosphere to obtain dark gray electrically conductive zinc oxide powder. Its powder resistivity was 1.1×10^{1} ohm·cm and the yield of the product was 58.6%.

The results were listed in the following TableⅡ.

Comparative Example 3

There were dissolved, in 296 ml of water, 52.34 g of zinc chloride(96%) and 4.20 g of aluminum chloride(95%). To the resulting solution there was gradually added 166 ml of 14% aqueous ammonia with stirring the solution at room temperature to raise the pH value of the liquid phase to 8.2. After the completion of the addition, the reaction

system was stirred for additional several minutes, followed by filtering off the resultant co-precipitates, washing the same and drying them at 100℃ for 15 hours. After preheating the precipitates at 450 ℃ for 1 hour in the air, the solid material or the precipitates were pulverized. The pulverized product was calcined at 800 ℃ for one hour in nitrogen gas atmosphere to obtain white powder mainly composed of zinc oxide. The powder resistivity thereof was not less than 10^8 omh·cm and the yuield of the product was 80%.

The results were listed in the following Table Ⅱ.

Comparative Example 4

(Significance of the Lower Limit of pH)

Electrically conductive powder of zinc oxide was prepared according to the same procedures as in Example 1 except that the neutralization reaction was performed while maintaining the pH value of the reaction system at 5. The powder resistivity thereof was 6.7×10^4 ohm·cm and the yield thereof was 76%. In addition, the content of chlorine was 5.5%.

The results were illustrated in the following Table Ⅱ.

Comparative Example 5

Electrically conductive powder of zinc oxide was prepared according to the same procedures as in Example 1 except that the temperature for calcining in a reducing atmosphere was established at 600 or 700℃. Volatilization of zinc oxide due to reduction was caused and the yield thereof was less than 80% in each case.

Ex. No.	Calcination Temp. (℃)	Powder Resistivity (ohm·cm)	Yield (%)	Color of the Product
5-1	600	1.2×10^1	73	dark gray
5-2	700	1.2×10^1	60	dary gray

The results were listed in the following TableⅡ.

Comparative Example 6

Electrically conductive powder of zinc oxide were prepared according to the same procedures as in Example 1 except that an alkaline solution was added to a zinc salt solution in one portion or in a manner of gradual addition (or step by step addition).

Ex. No.	Manner of addition	Powder Resistivity (ohm·cm)	Note
6-1	one portion addition	2.0×10^3	Cl content=2.5%
6-2	gradual addition	1.4×10^3	

The results were listed in the following TableⅡ.

Table I (Example)

Ex. No.	Zinc Compound	Alkali	Dopant: Combination		Dopant: Ratio of Addition %	Dopant: Ratio of Addition %	Reaction System: Temp. (℃)	Reaction System: pH	Drying Temp. ℃	Calcination: Temp. ℃	Calcination: Atmosphere	Calcination: Time min.	Product: Yield %	Product: Electric Conductivity (Ω · cm)	Color
1	$ZnCl_2$	NaOH	SnO_2	Ga_2O_3	0.593	0.545	60	10	105	500	H_2	60	98	1.8×10^0	White
2	〃	〃	〃	〃	〃	〃	〃	12	〃	〃	〃	〃	97.5	4.0×10^0	〃
3-1	〃	〃	〃	〃	0.500	0.400	〃	7		〃	〃	〃	99	1.2×10^0	〃
3-2	〃	〃	〃	〃	〃	〃	〃	8		〃	〃	〃	〃	5.0×10^0	〃
3-3	〃	〃	〃	〃	〃	〃	〃	9		〃	〃	〃	98	7.3×10^0	〃
3-4	〃	〃	〃	〃	0.005	0.005	〃	〃		〃	〃	〃	〃	5.1×10^0	〃
3-5	〃	〃	〃	〃	0.010	0.010	〃	〃		〃	〃	〃	〃	2.8×10^0	〃
3-6	〃	〃	〃	〃	0.020	0.020	〃	〃		〃	〃	〃	〃	4.2×10^0	〃
3-7	〃	〃	〃	〃	0.200	0.050	〃	〃		〃	〃	〃	〃	2.1×10^0	〃
3-8	〃	〃	〃	〃	0.500	0.400	〃	〃		400	〃	〃	99	7.4×10^{-1}	〃
3-9	〃	〃	〃	〃	〃	〃	〃	〃		450	〃	〃	〃	7.6×10^{-1}	〃
3-10	〃	〃	〃	〃	0.200	0.050	〃	〃		400	〃	〃	〃	2.8×10^0	〃
3-11	〃	〃	〃	〃	〃	〃	〃	〃		450	〃	〃	〃	1.5×10^0	〃
3-12			〃	〃	〃	〃	〃	〃		550	〃	〃	96	2.5×10^0	〃
3-13	$ZnCl_2$	Na_2CO_3	〃	〃	0.500	0.400	〃	6		500	〃	〃	96	4.7×10^1	〃
3-14	〃	NH_4OH	〃	〃	0.200	0.050	〃	6		〃	〃	〃	86	3.7×10^0	〃
3-15	$ZnSO_4$	NaOH	〃	〃	〃	〃	〃	8		〃	〃	〃	98	3.2×10^1	〃
3-16	〃	Na_2CO_3	〃	〃	〃	〃	〃	6		〃	〃	〃	96	3.7×10^1	〃
3-17	〃	NH_4OH	〃	〃	〃	〃	〃	7		〃	〃	〃	88	8.7×10^1	〃
3-18	$ZnCl_2$	NaOH	—	〃	〃	0.200	〃	7		〃	〃	〃	98	5.9×10^1	〃
3-19	〃	〃	—	〃	〃	0.050	〃	〃		〃	〃	〃	98	7.5×10^1	〃
3-20	〃	Na_2CO_3	Al_2O_3	〃	0.500	0.500	〃	6.5		〃	〃	〃	96.5	9.6×10^1	〃
3-21	〃	〃	〃	In_2O_3	1.000	0.300	〃	6.5		〃	〃	〃	96	7.1×10^1	〃

Table II (Comparative Examples)

Comparative Example No.	Zinc Compound	Alkali	Activator				Reaction System		Drying Temp. ℃
			Combination		Ratio of Addition		Temp. ℃	pH	
1	$ZnCl_2$	Na_2CO_3	SnO_2	Al_2O_3			80		
2	〃	〃	$SnO_2/Al_2O_3/Ga_2O_3$				〃		500
3	〃	NH_4OH	—	Al_2O_3			100	8.2	100
4	〃	NaOH	SnO_2	Ga_2O_3	0.593	0.545	60	5	105
5- 1	〃	〃	〃	〃	〃	〃	〃	10	〃
5- 2	〃	〃	〃	〃	0.005	〃	〃	10	〃
6- 1	〃	〃	〃	〃	0.010	〃	〃		〃
6- 2	〃	〃	〃	〃	0.020	〃	〃		〃

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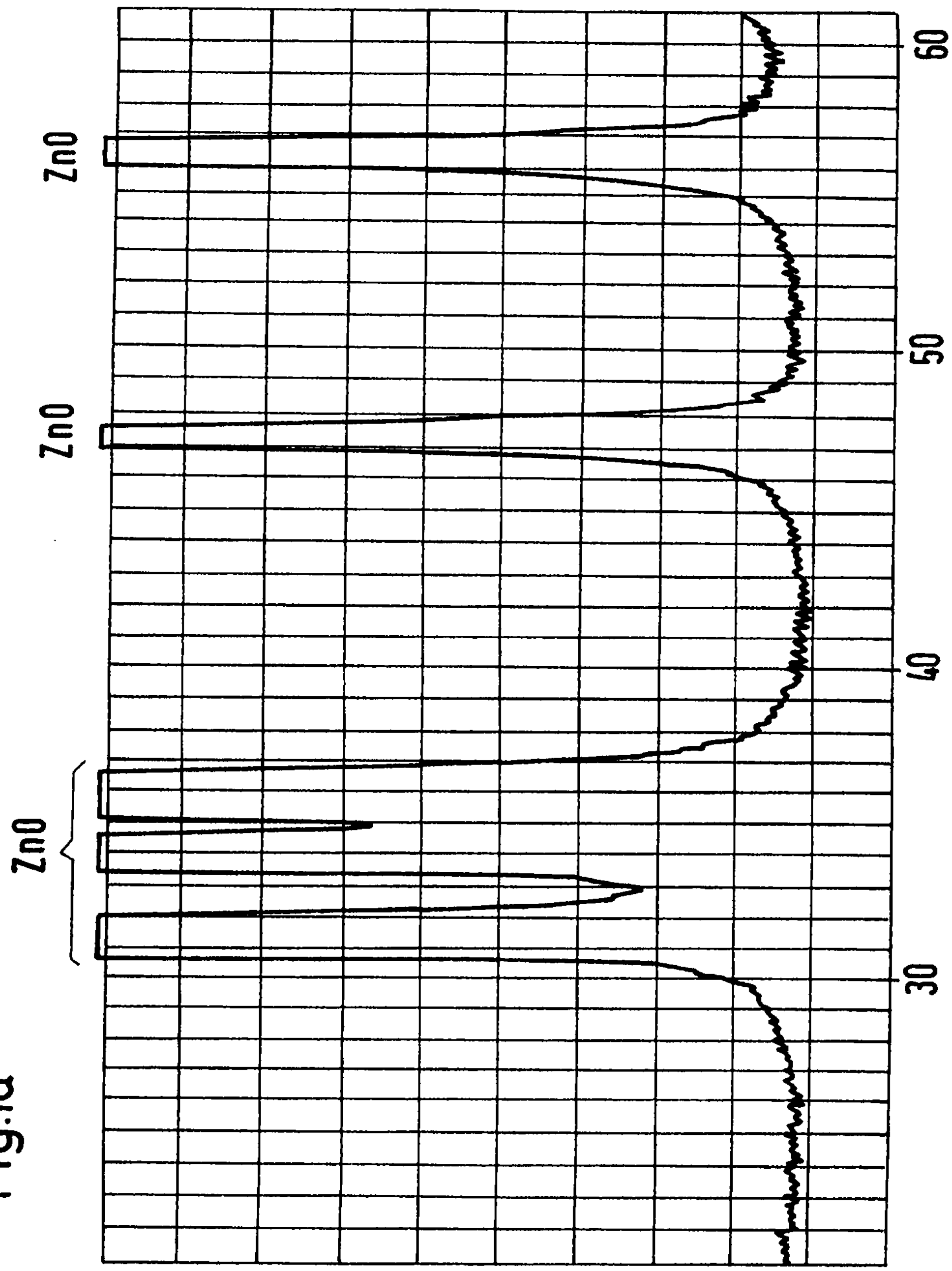
Fig.1a



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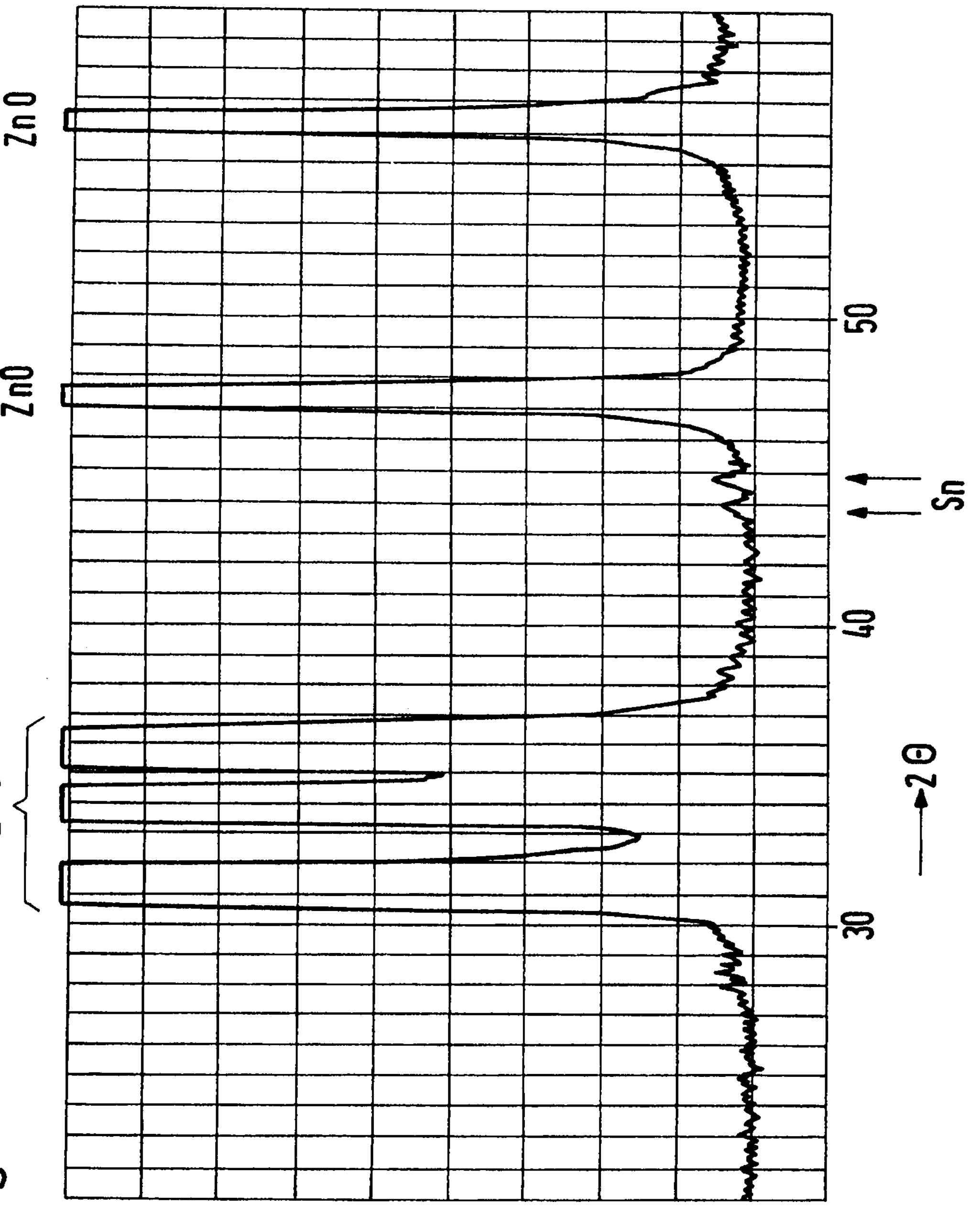

Fig.1b

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